

# Numerical simulation of the thermal fragmentation process in fullerene C<sub>60</sub>

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## ABSTRACT

The processes of defect formation and annealing in fullerene C<sub>60</sub> at  $T = (4000 - 6000)$  K are studied by the molecular dynamics technique with a tight-binding potential. The cluster lifetime until fragmentation due to the loss of a C<sub>2</sub> dimer has been calculated as a function of temperature. The activation energy and the frequency factor in the Arrhenius equation for the fragmentation rate have been found to be  $E_a = (9.2 \pm 0.4)$  eV and  $A = (8 \pm 1) \cdot 10^{19} \text{ s}^{-1}$ . It is shown that fragmentation can occur after the C<sub>60</sub> cluster loses its spherical shape. This fact must be taken into account in theoretical calculations of  $E_a$ .

In spite of intensive experimental and theoretical studies of fullerene C<sub>60</sub> [1], there is still controversy concerning some of its physical and chemical characteristics. In particular, a significant discrepancy between theory and experiment in the determination of the energy  $D$  required for the loss of a C<sub>2</sub> dimer from fullerene C<sub>60</sub> was repeatedly noted until the late 1990s. Calculations performed using the most accurate *ab initio* methods gave the value  $D = (11 - 12)$  eV [2] (see also one of the most recent theoretical works [3]), which exceeded the experimental value of  $D = (5 - 8)$  eV by a factor of 1.5 - 2; see references in [4]. Note, however, that the fragmentation (dissociation) energy was calculated theoretically by the equation

$$D = E(\text{C}_{58}) + E(\text{C}_2) - E(\text{C}_{60}), \quad (1)$$

where  $E(C_n)$  is the energy of the corresponding clusters, while  $D$  in the analysis of experimental data was usually assumed equal to the activation energy  $E_a$  [4] entering into the Arrhenius equation for the fragmentation rate

$$k(T) = A \cdot \exp(-E_a/k_B T), \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $A$  is the frequency factor in s<sup>-1</sup>. It should be noted here that the fragmentation energy  $D$  and the activation energy  $E_a$ , generally speaking, have a different physical meaning; therefore, their comparison is not quite straightforward.

When  $E_a$  was determined by Eq. (2), it was commonly assumed that  $A \sim 10^{15}$  s<sup>-1</sup> as in the majority of mid-size clusters. More recently, it has been shown in a series of publications [4 - 7] that the value of  $A$  for fullerene C<sub>60</sub> can be much higher than had been considered previously,  $A \sim (10^{19} - 10^{20})$  s<sup>-1</sup>. Assuming that  $A = 5 \cdot 10^{19}$  s<sup>-1</sup>, the authors of [7] reanalyzed the results of a great number of experiments and came to the conclusion that  $E_a = (10.5 \pm 0.2)$  eV, where

the arithmetic mean and the standard error were calculated with "improved" experimental values. This new corrected value of  $E_a$  is in much better agreement with both the theoretical value of  $D$  [2, 3] and the more recent experimental data [8 - 13]. However, when revising the experiments carried out in the past years, the authors of [7], for various reasons, excluded from their statistical treatment a number of publications in which the activation energy  $E_a$  proved to be substantially lower than 10 eV even after its recalculation with a different frequency factor. Moreover, the choice of the value  $A = 5 \cdot 10^{19} \text{ s}^{-1}$  in [7] (or  $A = 2 \cdot 10^{19} \text{ s}^{-1}$  and even  $A = 3.4 \cdot 10^{21} \text{ s}^{-1}$  in the subsequent publications [9, 10, 12]) seems to be somewhat artificial. This leaves a certain feeling of disappointment and looks like an attempt to fit the experiment to theory.

It is also appropriate to note the following circumstance. In the calculation of the fragmentation energy  $D$  of fullerene  $C_{60}$  by Eq. (1), it was suggested that both the initial cluster and its dissociation product ( $C_{58}$  cluster) are in their optimal (most energy-favorable) configurations with the lowest possible energy  $E(C_n)$  at a given number of carbon atoms in the cluster ( $n = 60$  or  $58$ ). This corresponds to so-called adiabatic dissociation. At the same time, under real conditions, the  $C_2$  dimer can be detached from a  $C_{60}$  cluster which is (at least) strongly distorted due to an external action and/or thermal vibrations rather than from the perfect fullerene. The structure of the  $C_{58}$  cluster remaining after the evaporation of the  $C_2$  dimer can also differ from the most stable one (standard mass-spectrometry methods can determine the number of atoms in a cluster but not its shape).

From all the above, it follows that a real-time numerical simulation of fullerene  $C_{60}$  fragmentation is of great interest. It allows the temperature dependence of the cluster lifetime

$$\tau(T) = \frac{1}{k(T)} \quad (3)$$

to be determined directly and the values of  $A$  and  $E_a$  to be found from Eq. (2) without any additional assumptions. The results of simulations of fullerene  $C_{60}$  dynamics at high temperature have been presented previously in a number of works. In this case, however, the main attention has been paid to studying phase transformations upon heating the cluster [14 - 16] or the mechanism of  $C_2$  dimer loss from the cluster [17 - 19]. In the present work, all the steps of fullerene  $C_{60}$  fragmentation are studied, starting with the formation of defect isomers and ending with the loss of a  $C_2$  dimer. We used tight-binding molecular dynamics [20], in which the many-body tight-binding potential allowed the electronic subsystem contribution to the total energy to be determined more accurately than in the case of simple classical potentials. This potential did not require such a large expenditure of computer resources as *ab initio* approaches, thus making it possible to follow the evolution of fullerene  $C_{60}$  during  $t \approx 20$  ns (while usually  $t < .1$  ns in *ab initio* calculations). At the same time, for bond lengths, binding energies, the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap), potential barrier heights in the Stone-Wales transformation [21], and other characteristics of fullerene  $C_{60}$ , the tight-binding potential gives values that are in good agreement with experimental data and/or *ab initio* calculations (for more details, see [19]). Using Eq. (1) and this potential, we calculated the most energy-favorable configurations of  $C_{58}$  and  $C_{60}$  clusters and obtained  $D = 11.04$  eV, which is also in agreement with theoretical data available in the literature [2, 3].

The numerical simulation of fullerene  $C_{60}$  dynamics was performed at a fixed total energy of the cluster [22]. This approach to the problem corresponds to a real experimental situation in the fragmentation of fullerenes when clusters excited by a laser pulse do not collide with each other during the time  $t < 1 \mu s$  required for their fragmentation; that is, they are

not in thermal equilibrium with the environment (see [17]). In this case, the cluster temperature  $T$  is a measure of the relative motion of its constituent atoms, that is, a measure of the excitation energy after irradiation with a laser. It was determined by the equation  $\frac{1}{2}k_B T(3n - 6) = \langle E_{\text{kin}} \rangle$ , where  $n = 60$ , and  $\langle E_{\text{kin}} \rangle$  is the kinetic energy averaged over  $10^3 - 10^4$  molecular-dynamics steps (the time of one step is  $t_0 = 0.272$  fs). At the initial time, random velocities and displacements were imparted to all the atoms so that the total momentum and angular momentum were equal to zero. The forces acting on the atoms were calculated by the Hellmann-Feynman theorem using the tight-binding Hamiltonian. After that, the classical Newtonian equations of motion were solved numerically.

Since the total energy, that is, the sum of the kinetic and potential ( $E_{\text{pot}}$ ) energies, remains constant in the process of cluster evolution, its temperature  $T$  (as a measure of the kinetic energy) decreases when the cluster transforms to a metastable state with a higher value of  $E_{\text{pot}}$  [a lower binding energy  $E_b = 60E_{\text{pot}}(1) - E_{\text{pot}}(60)$ ] and increases in the opposite case. The dependence of  $T$  on time  $t$  is presented in Fig. 1a at the initial temperature  $T_{\text{ini}} = (4250 \pm 15)$  K. The dependence  $T(t)$  exhibits clearly defined steps. They are associated with the formation and annealing of defect isomers obtained from fullerene  $\text{C}_{60}$  and from each other as a result of the so-called Stone-Wales transformation [23], which represents a transposition of two C-C bonds. While carbon atoms in initial fullerene  $\text{C}_{60}$  are located at the vertices of twenty hexagons and twelve pentagons isolated from each other, the first Stone-Wales transformation at  $t \approx 2.2$  ns gives an isomer containing two pairs of pentagons with common sides. Its potential energy is higher than that of fullerene  $\text{C}_{60}$  by  $\Delta E_{\text{pot}} = 1.42$  eV [19]. As a consequence, the cluster temperature drops stepwise by  $\Delta T \approx 100$  K. If each pair of neighboring pentagons is considered as one 5/5 defect, then this isomer contains  $N_{5/5} = 2$

such defects (for other defect isomers, the value of  $E_{pot}$  is higher; no isomer with  $N_{5/5} = 1$  exists for topological reasons).

At  $t \approx 2.7$  ns, the temperature drops again by  $\Delta T \approx 100$  K. An analysis of the structure of the cluster showed that an isomer with  $N_{5/5} = 4$  forms in this case. Then (at  $t \approx 3.1$  ns), one defect and, almost immediately, another one are annealed. As a result, an isomer with  $N_{5/5} = 2$  forms again. After annealing of all defects, the structure of the initial fullerene  $C_{60}$  is restored at  $t \approx 4.4$  ns. This structure is retained up to  $t \approx 7.6$  ns, after which a sequence of transitions starts, leading eventually to the loss of the  $C_2$  dimer at  $t \approx 9.5$  ns; see Fig. 2a. Note that a nonclassical fullerene forms at  $t \approx 7.9$  ns that contains one heptagon along with penta- and hexagons, and tetragons appear subsequently. The  $C_{58}$  cluster that forms after fragmentation also represents a metastable isomer of fullerene  $C_{58}$ . It contains  $N_{5/5} = 6$  pairs of neighboring pentagons, while  $N_{5/5} = 3$  in fullerene  $C_{58}$  with the lowest possible energy.

Though the  $C_2$  dimer in the above example of fullerene  $C_{60}$  fragmentation is detached from a strongly defect  $C_{60}$  cluster, this cluster still has a closed spherical shell; see Fig. 2a. The  $C_{58}$  cluster forming as a result of fragmentation also has the same shape. However, our analysis showed that this is not necessarily the case. We will give an alternative example. The dependence  $T(t)$  at  $T_{ini} = (4335 \pm 10)$  K is presented in Fig. 1b. The narrow deep minimum in  $T(t)$  at  $t \approx 1.6$  ns is associated with the formation and rapid annealing (within  $\Delta t \approx 0.1$  ns) of an isomer containing a dodecagon along with a heptagon. Actually, the cluster in this case opens for a short time, and a large window appears on its surface. The same occurs at  $t \approx 3.6$  and at  $t \approx 4.8$  ns. The next time, such a window forms at  $t \approx 5.2$  ns; however, now it adjoins two heptagons rather than one. In addition, the cluster also has two pairs of neighboring pentagons. The closed surface is not restored up to the loss of the  $C_2$  dimer from

the cluster. The  $C_{58}$  cluster remaining after fragmentation is also opened, see Fig. 2b.

Since the fragmentation of fullerene  $C_{60}$  is of stochastic character, it is reasonable to consider the mean lifetime  $\tau$  at a certain temperature rather than the fragmentation temperature [24]. In order to collect statistical data sufficient for determining the temperature dependence of  $\tau$ , we performed calculations at several tens of values of  $T_{ini} = 4000 - 6000$  K corresponding to various sets of initial velocities and displacements. We found correlation between  $T_{ini}$  and the character of the  $C_{60}$  cluster distortion immediately before fragmentation. The cluster before fragmentation is more frequently opened than closed at  $T_{ini} > 5000$  K and the other way around at  $T_{ini} < 5000$  K. Although the fragmentation proceeded by means of the loss of a  $C_2$  dimer in the majority of cases, the evaporation of either one carbon atom, or a  $C_3$  trimer, or a  $C_4$  tetramer occurred several times, as was also observed experimentally [25]. With the aim of comparing the results of simulations with experiments on the loss of a  $C_2$  dimer, we retained for analysis only variants in which fragmentation proceeded through the channel  $C_{60} \rightarrow C_{58} + C_2$ . In order to take into account the effects due to the small cluster size and the absence of heat exchange with the environment, we used the following equation for the fragmentation rate instead of Eq. (2):

$$k(T) = A \cdot \exp \left[ -\frac{E_a}{k_B T \left( 1 - \frac{E_a}{2CT} \right)} \right]. \quad (4)$$

This equation is derived from the finite-heat-bath theory in the first-order approximation with respect to the small parameter  $E_a/2CT$  [26, 27]. Here,  $C$  is the microcanonical heat capacity of the cluster. We assumed that  $C = (3n - 6)k_B$ , where  $n = 60$ . Since  $E_a/2CT \approx 0.07$  at  $T \approx 5000$  K, the possible difference between  $C$  and  $(3n - 6)k_B$  does not lead to any significant error in the determination of  $E_a$  from Eq. (4).

The calculated dependence of the logarithm of the fullerene lifetime  $\tau = 1/k$  on is presented

in Fig. 3, where  $T_{ini}^* = T_{ini}(1 - E_a/2CT_{ini})$ , see Eq. 4. In a rather wide range of  $T_{ini} = (4000 - 6000)$  K and, correspondingly,  $\tau = 1$  ps - 20 ns, the results of numerical simulation are described well by Eq. (4) with  $A = \text{const}(T)$ . The statistical scatter of the data prevents the temperature dependence of  $A$  from being reliably determined. However, it may be argued, in any case, that this dependence is sufficiently weak in this range of  $T_{ini}$ , since the dependence of  $\ln(\tau)$  on  $(T_{ini}^*)^{-1}$  is approximated well by a straight line, see Fig. 3. The activation energy  $E_a$  and the frequency factor  $A$  can be determined by the slope of this line and the point of its intersection with the ordinate axis. For the mean values and standard errors of these quantities, we obtained  $E_a = (9.2 \pm 0.4)$  eV and  $A = (8 \pm 1) \cdot 10^{19} \text{ s}^{-1}$  (since  $E_a$  enters both into the numerator of the exponent in Eq. (4) and into the renormalized initial temperature, it was determined self-consistently by successive iterations).

Previously, ideas of the loss of a  $\text{C}_2$  dimer from a strongly defect  $\text{C}_{60}$  cluster were discussed as a hypothesis for the explanation of the discrepancy between the values of  $D$  and  $E_a$  [25]. However, these considerations were not confirmed by the corresponding calculations (though evidence for the two-step character of fullerene  $\text{C}_{60}$  fragmentation was obtained in [28] using the semiempirical Tersoff potential). Note that the value of  $E_a$  found in our work is somewhat lower than the averaged experimental value  $E_a = (10.5 \pm 0.2)$  eV [7]. However, if the experiments giving  $E_a < 10$  eV were not rejected, as was done by the authors of [7], the experimental mean value  $E_a = (8-9)$  eV would almost coincide with our result. We emphasize the fact that the value of the frequency factor  $A$  found in our work by direct calculations without any assumptions is in reasonable agreement with the values  $A = (2 - 5) \cdot 10^{19} \text{ s}^{-1}$ , which have been used in recent years by the majority of authors in the analysis of experimental data [7, 9, 11-13], and does not strongly differ from the value  $A \sim 10^{21} \text{ s}^{-1}$  reported in the

most recent publication in this field [29].

Note in conclusion that it is interesting to calculate the lifetime of fullerene  $C_{60}$  at lower temperatures  $T = (1000 - 4000)$  K and possibly to determine the temperature dependence of the frequency factor. With molecular dynamics, this task, however, is beyond the possibilities of the present-day computational technique. For its solution, fundamentally different approaches are required based, for example, on Monte Carlo algorithms.

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## Figure captions

Fig. 1. Time dependence of the fullerene  $C_{60}$  temperature obtained by numerical molecular dynamics simulations. The total energy of the cluster is constant, and the time of one step is  $t_0 = 0.272$  fs. The values of  $T$  were calculated by averaging the kinetic energy over  $10^4$  steps. The initial temperature  $T_{ini} =$  (a)  $(4250 \pm 15)$  K and (b)  $(4335 \pm 10)$  K. The sequence of the formation and annealing of defect  $C_{60}$  isomers leading to the loss of a  $C_2$  dimer is as follows:  $C_{60} \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60}(N_{5/5} = 4) \rightarrow C_{60}(N_{5/5} = 3) \rightarrow C_{60}(N_{5/5} = 4) \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60} \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60}(N_{5/5} = 4, N_7 = 1) \rightarrow C_{60}(N_{5/5} = 6, N_7 = 1) \rightarrow C_{60}(N_{5/5} = 7, N_7 = 1) \rightarrow C_{60}(N_{5/5} = 9, N_7 = 2) \rightarrow C_{60}(N_{5/5} = 4, N_7 = 1, N_4 = 1) \rightarrow C_{60}(N_{5/5} = 6) \rightarrow C_{60}(N_{5/5} = 4, N_7 = 1, N_4 = 1) \rightarrow C_{58} + C_2$  for (a) and  $C_{60} \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60} \rightarrow C_{60}(N_7 = 1, N_{12} = 1) \rightarrow C_{60} \rightarrow C_{60}(N_7 = 1, N_{12} = 1) \rightarrow C_{60} \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60}(N_{5/5} = 4, N_7 = 1) \rightarrow C_{60} \rightarrow C_{60}(N_{5/5} = 4, N_7 = 1) \rightarrow C_{60}(N_{5/5} = 2) \rightarrow C_{60}(N_{5/5} = 5, N_7 = 1) \rightarrow C_{60}(N_{5/5} = 4, N_7 = 2, N_{12} = 1) \rightarrow C_{58} + C_2$  for (b), where  $N_{5/5}$ ,  $N_4$ ,  $N_7$ , and  $N_{12}$  are the numbers of pairs of pentagons with common sides, tetragons, heptagons, and dodecagons, respectively; see text.

Fig. 2. Snapshots of a  $C_{60}$  cluster before and immediately after fragmentation. The time interval between two snapshots is  $\Delta t \approx 2$  ps. For clarity, the distant atoms are not shown. The atoms removed upon fragmentation are shown in black. The temperature prehistory of fragmentation processes (a) and (b) are given in Figs. 1a and 1b, respectively.

Fig. 3. Logarithm of the lifetime  $\tau$  (in seconds) of fullerene  $C_{60}$  before  $C_{60} \rightarrow C_{58} + C_2$  fragmentation vs. the reciprocal initial temperature (kelvins) including the finite-heat-bath correction, see text. The circles are the results of calculations and the solid line is a linear least-squares approximation.

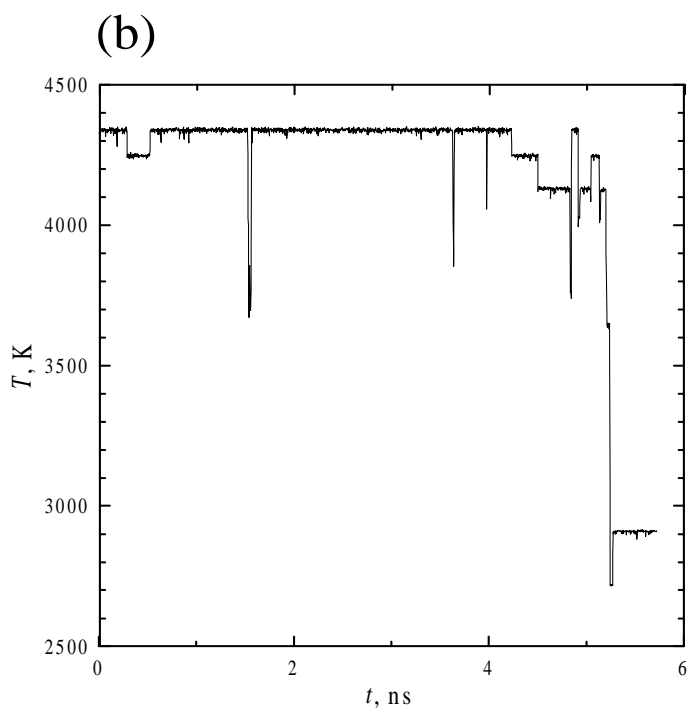
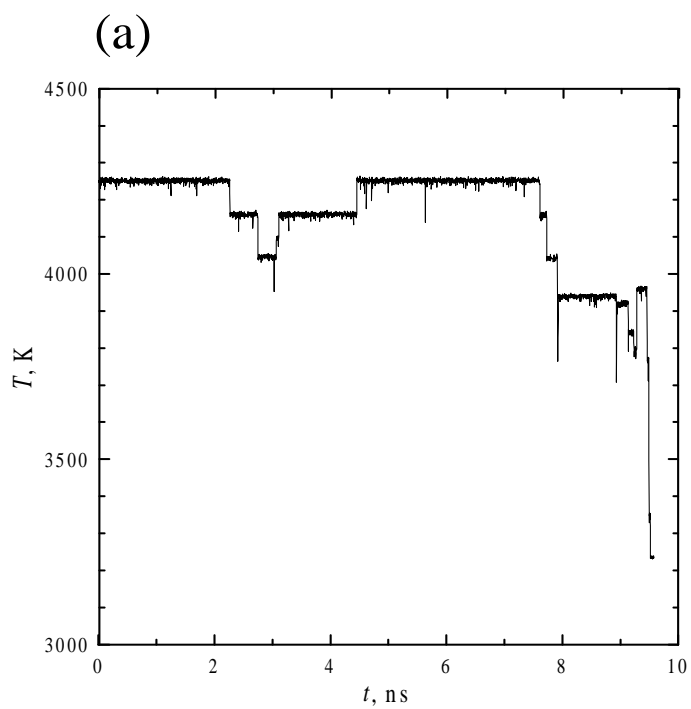


Figure 1

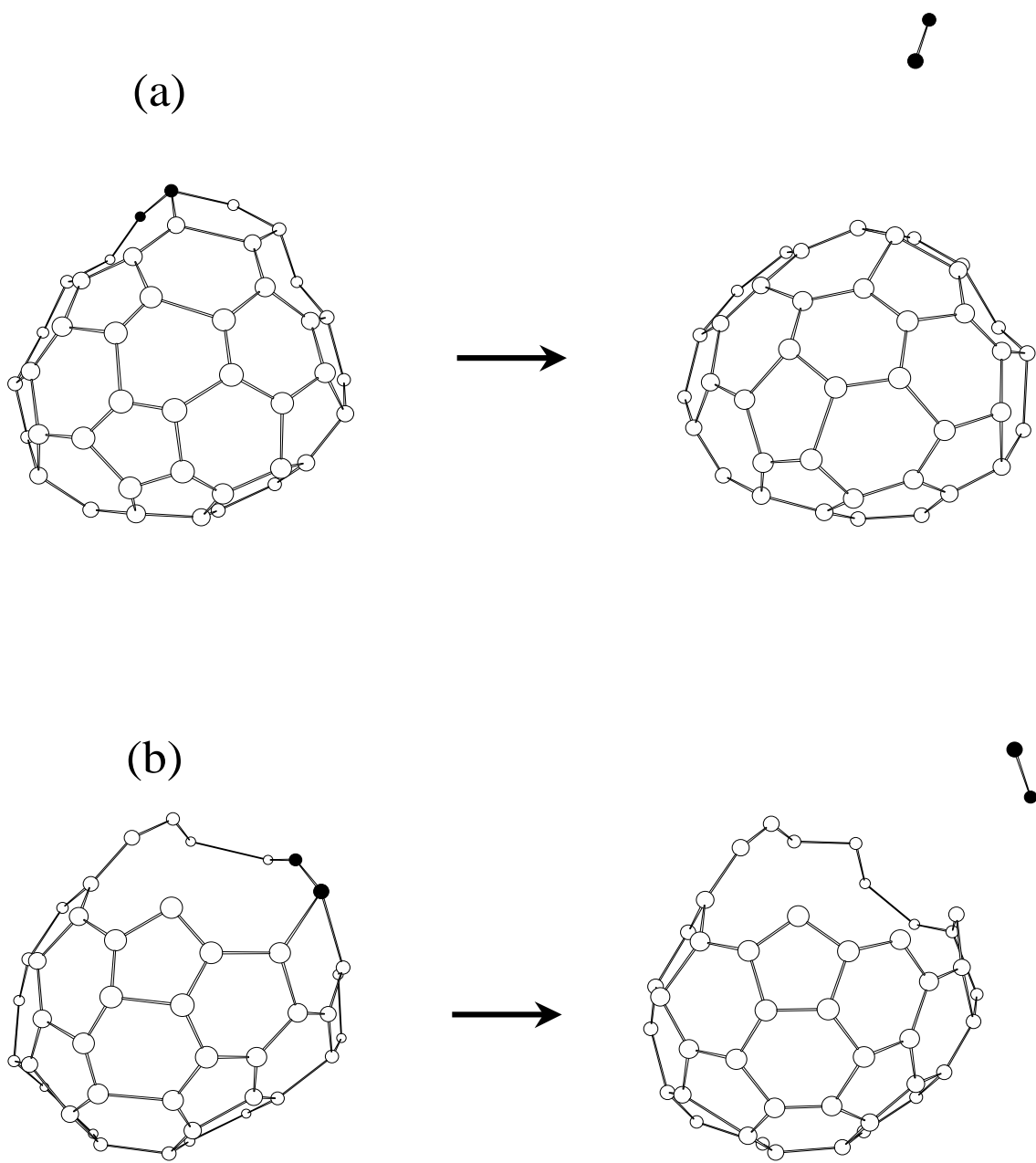


Figure 2

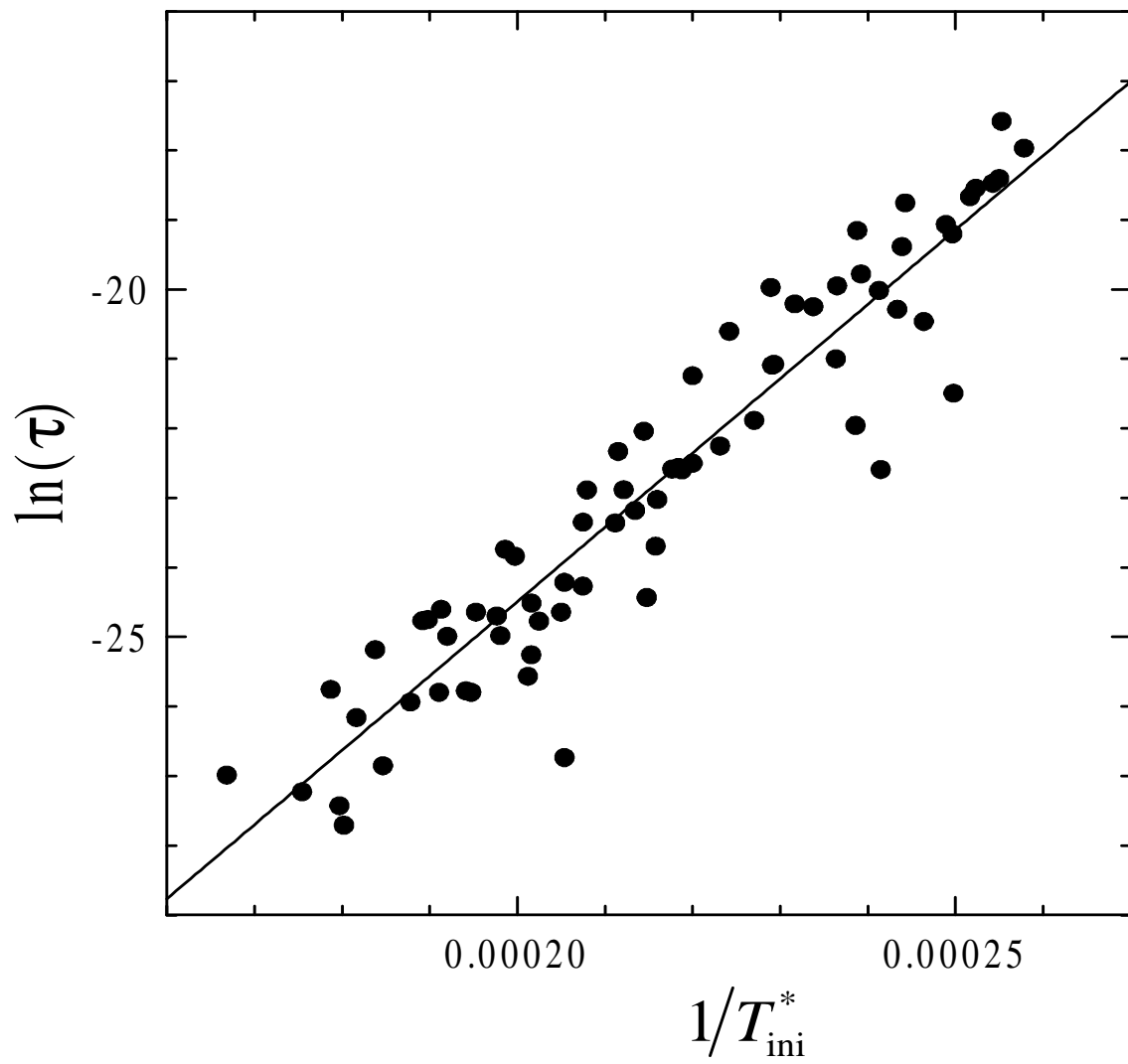


Figure 3